

Sequence randomness and polymer collapse transitions.

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Contrary to expectations based on Harris' criterion, chain disorder with frustration can modify the universality class of scaling at the theta transition of heteropolymers. This is shown for a model with random two-body potentials in 2D on the basis of exact enumeration and accurate Monte Carlo results. When frustration grows beyond a certain finite threshold, the temperature below which disorder becomes relevant coincides with the theta one and scaling exponents definitely start deviating from those valid for homopolymers.

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In recent years, work on polyampholytes and on biomolecules, like proteins, has focused much attention on the conformational properties of inhomogeneous polymeric chains (heteropolymers) [1]. Some of these properties, like protein folding, are expected to be determined by the specific sequence of different monomers constituting the chain [2]. In this context, particularly relevant is a statistical point of view, according to which the behavior of large ensembles of different sequences is globally tested with philosophy and methods of the physics of quenched disordered systems [3]. Such studies are intended to provide information on the conditions under which specificity becomes important (i.e., disorder becomes relevant) and to give global descriptions of its possible effects.

The collapse from swollen to compact globular state of a long macromolecular chain is by now well understood in the case of homopolymers. At temperature T , a chain with $N \gg 1$ equal monomers has an average radius of gyration $R_N \propto N^{\nu(T)}$. $\nu(T)$ is equal to the exponent of a self-repelling chain (SAW) [4] for all temperatures $T > T_\theta$, and to $1/d$ for $T < T_\theta$, as appropriate for a compact object. $\nu(T_\theta) = \nu_\theta$ has a distinct, intermediate value, known both in 3D (1/2) [5] and in 2D (4/7) [6]. This transition is triggered by attractive interactions between monomers as T decreases. In the case of heteropolymers, the theta transition involves the same sequence of regimes and preludes to the folding phenomenon, for which specificity is surely of key importance. Thus, one can wonder if chain disorder could substantially affect polymer behavior already at the onset of theta collapse, or even at higher T .

Unlike random environment disorder for a homopolymer, if amounting to a small perturbation, inhomogeneities in the structure of the chain should in general be expected to be irrelevant and not able to affect the ordered system's behavior, as far as universal scaling is concerned. This is suggested by Harris' criterion [7] as we discuss below. In fact, contrary to previous conjectures [8], recent work on a model of randomly charged polymers in 2D and 3D, has shown that disorder does not change

the universality class of the theta transition [9], consistent with the most simple scenario one could infer based on application of the above criterion. However, in this Letter we give evidence that sufficiently large amounts of chain disorder and frustration can modify the heteropolymer theta behavior, with respect to the homopolymer one. Thus, in such situations, chain specificity becomes a key ingredient in determining the universality class of the theta point. Quite remarkably, this point seems to fall right at the upper limit of temperatures for which disorder plays a relevant role.

As heteropolymer model we consider here an N -step SAW on square lattice. On each lattice site visited by the walk sits a monomer. Monomers i and j ($0 \leq i, j \leq N$) which are not consecutive along the chain ($i \neq j$, $|j - i| \neq 1$) and occupy nearest neighbor lattice sites in a given configuration, feel an attractive potential V_{ij} (i and j constitute a contact indicated by $\langle ij \rangle$). V_{ij} is random with probability distribution $P(V_{ij}) = p\delta(V_{ij} + V) + (1-p)\delta(V_{ij} - V)$, ($V < 0$). Its values are assigned independently to each pair of monomers along the sequence. Models of this kind were already used for proteins [3]. We choose it here because, since disorder is associated to monomer pairs, rather than to individual monomers, the annealed partition can be easily mapped into a well defined effective homopolymer problem.

One has to compute free energy and other thermal averages for each possible potential arrangement along the sequence. Results have then to be further averaged over disorder. In addition one wants to establish how important fluctuations due to different disorder configurations are in the evaluation of the final results. A typical case is that of the free energy: the quenched quantity is the disorder average of the logarithm of the partition function, $Z_N\{V\} = \sum_{\omega} \exp(-\sum_{\langle ij \rangle \in \omega} V_{ij}/T)$, where the number of steps of all the chain configurations ω is implicitly assumed equal to N . If the distribution of Z_N values is sharply peaked around its disorder average, $\overline{Z_N} = \sum_{\{V\}} \Pi_{\langle ij \rangle} P(V_{ij}) Z_N\{V\}$, we have

$\ln(\overline{Z_N}) = \overline{\ln(Z_N)}$ for $N \rightarrow \infty$, and disorder plays no role, i.e. annealed and quenched free energies, respectively, are identical.

Since the potentials for different $\langle ij \rangle$ are independent random variables, the annealed problem reduces to a standard homopolymer one with an effective attractive interaction $-T \log(\overline{\exp(-V_{ij}/T)})$. Imagine now to perturb with a slight disorder ($p \sim 0$) the attractive homopolymer situation ($p = 1$, $V_{ij} = -V$). The possible relevance of disorder can then be discussed by looking at n replicas of the SAW, for which the average partition can be put in the form:

$$\overline{Z_N^n} = \sum_{\omega_\alpha, \alpha=1, \dots, n} \exp \left[-\frac{1}{T} \sum_{\beta} \sum_{\langle ij \rangle \in \omega_\beta} \overline{V_{ij}} + \right. \\ \left. -\frac{1}{2T^2} \sum_{\gamma, \delta} \sum_{\langle kl \rangle \in \omega_\gamma} \sum_{\langle mn \rangle \in \omega_\delta} \overline{\delta V_{kl} \delta V_{mn}} + \dots \right] \quad (1)$$

where a cumulant expansion has been used for disorder averages, and $\overline{V_{ij}} = V(1 - 2p)$, while $\overline{\delta V_{ij} \delta V_{kl}} = 4p(1 - p)\delta_{i,l}\delta_{j,k}$. Thus, if $\overline{V_{ij}}/T$ is fixed to the value appropriate for the renormalization group fixed point of a homopolymer at the theta transition, according to eq.1 the leading perturbation to this fixed point is given by an operator proportional to the number $I(\omega_\gamma, \omega_\delta)$ of distinct contacts common to two replicas in configurations ω_γ and ω_δ [10]. The relevance or irrelevance of the disorder perturbation depends on whether, for the two replicas, the average of I grows with N , or not. By exact enumeration we studied this average for two replicas of up to 19 steps without mutual interactions, and verified to high precision that indeed, at the theta point, or even at lower temperatures, it saturates to a constant for growing N . This implies irrelevance and could lead to expect that also finite amounts of disorder would not be sufficient to subtract the theta transition from the control of the homopolymer fixed point. In such a scenario the border line temperature, T_d , below which disorder becomes possibly relevant, should always satisfy $T_d < T_\theta$ strictly.

To determine T_d is highly nontrivial. A straightforward strategy could consist in extrapolating the ratio $\overline{Z_N^2}/\overline{Z_N}^2$ to $N \rightarrow \infty$. According to general theorems [11], if this ratio tends to some finite $B \geq 1$, the annealed free energy should be obtained for a fraction of all sequences summing up to a probability $\geq 1/B$. Thus, if $B = 1$, quenched and annealed problems must coincide. B is in principle adequate only to establish an upper bound on T_d . In addition, since quantities like $\overline{Z_N}$ are wildly diverging and sensibly oscillating for increasing N , B estimates are problematic and we have to use a different strategy [9]. Besides ν , also entropic exponents characterize SAW scaling. For example, one expects $\overline{Z_N} \sim N^{\gamma_a - 1} K_a^{-N}$ for $N \rightarrow \infty$ [4]. γ_a must take on the distinct values (appropriate for homopolymers) 43/32 and 8/7, for $T > T_{a\theta}$ and $T = T_{a\theta}$ [4,6],

respectively, where $T_{a\theta}$ indicates the theta temperature of the annealed problem. For $T < T_{a\theta}$ the precise value of γ_a is still debated and may be non-universal, depending on lattice and boundary conditions [12]. If the polymer has one end fixed on an impenetrable boundary in semi-infinite geometry, the behavior of the corresponding partition function, $\overline{Z_{1N}}$, changes only to the extent that γ_a is replaced by a boundary exponent γ_{1a} , while the exponential growth has the same K_a [4,13]. Thus, $\overline{Z_N}/\overline{Z_{1N}}$ grows as $N^{\gamma_a - \gamma_{1a}}$, which is more easy to extrapolate [14]. If one assumes for the quenched free energies $\exp(\log(\overline{Z_N}))$ and $\exp(\log(\overline{Z_{1N}}))$ similar behaviors with exponents γ and γ_1 , respectively, $\gamma - \gamma_1 = \gamma_a - \gamma_{1a}$ should hold for extrapolated differences, as long as annealed and quenched free energies coincide. The temperature at which the two differences possibly cease to be equal should be identified with T_d . If $T_{a\theta} > T_d$, one must also find $T_{a\theta} = T_\theta$ and all theta exponents in the annealed and quenched problems are the same. T_d determinations based on checking validity of $\gamma - \gamma_1 = \gamma_a - \gamma_{1a}$ are much more precise than those based on the analysis of exponential growths, and reveal of key importance for our investigation.

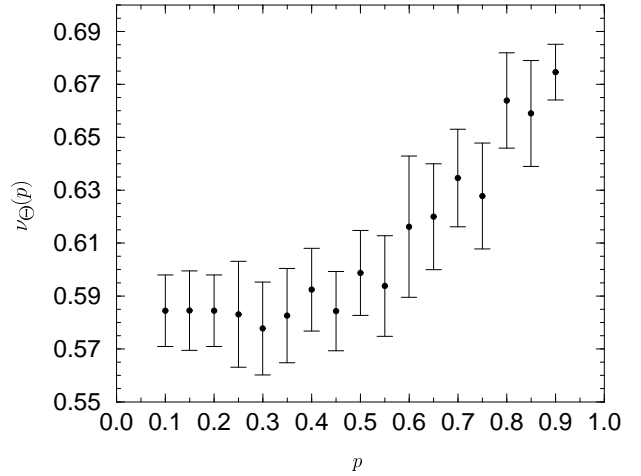


FIG. 1. Extrapolated ν_θ as a function of p . For details of these and other determinations see ref. [9].

The basic tool of our approach is the exact determination of all possible contact maps [15] for a polymer of N steps. The contact map in a given configuration ω is the set of contacts $\langle ij \rangle \in \omega$. After all maps have been sorted, since interactions pertain to contacts, the (entropic) free energy associated to each map can be evaluated exactly once for all, and used in order to perform relatively fast averages over the disorder affecting the interactions. This latter averaging could be performed either exactly, or by extensive Monte Carlo (MC) sampling (up to 2×10^4 potential configurations) for the longest chains considered here. Our contact map algorithm alone can treat chains of length exceeding by at least 4 steps the maximum length reached in most recent work [16].

We determined for N up to 22 and all T the averages

$$\overline{\langle R_N^2 \rangle} = \Sigma_{\{V\}} \Pi_{\langle ij \rangle} P(V_{ij}) \langle R_N^2 \rangle \{V\} \quad (2)$$

where $\langle R_N^2 \rangle \{V\}$ is the thermally averaged end-to-end distance for a particular $\{V\}$. $\overline{\langle R_N^2 \rangle}$ is expected to grow with $N \rightarrow \infty$ as a power law with the three exponent values mentioned above. We expect that effective exponents $\nu(M, K, T) = \frac{1}{2} \log(\langle R_M^2 \rangle / \langle R_{M-K}^2 \rangle) / \log(M / (M - K))$, should interpolate smoothly between values, which, for increasing M , approach the swollen and the compact ν exponents, for $T > T_\theta$ and $T < T_\theta$, respectively. If the trends of approach are monotonic and opposite in the two cases, it is also very likely to find that the various curves $\nu = \nu(M, K, T)$ bend quite rapidly and intersect with each other in a narrow region of the (T, ν) plane, each intersection representing an approximate determination of the asymptotic ν_θ . In fact the pattern of T -dependence we found for $\nu(M, K, T)$ is of this kind for all values of p we tested. We identified T_θ as the center of the relatively narrow T range within which the trend of various $\nu(M, K, T)$ changes from monotonically increasing, to monotonically decreasing with M . This can be done by use of suitable data correlators [9]. ν_θ is then determined by extrapolation of $\overline{\langle R_N^2 \rangle}$ at T_θ . Figs.1 and 2 show determinations of ν_θ and T_θ , respectively. $T_{a\theta}$ is known with high precision based on the mapping of the annealed problem onto the effective homopolymer one (Fig.2). T_θ remains remarkably close to $T_{a\theta}$ in the whole range $0 < p < 1$. This means that T_d should never overcome T_θ , even for very large p 's. That $T_d > T_\theta$ should be ruled out is rather plausible, since sequence disorder is very unlikely to affect the swollen phase. On the other hand, the behavior of ν_θ as a function of p is pretty stable and nicely consistent with the homopolymer universality class ($\nu_\theta \sim 4/7$) only for $p \leq 0.50 \div 0.55$. For larger p 's ν_θ starts deviating rather markedly ($\nu_\theta \sim 0.64$) from $4/7$ and increases up to ~ 0.68 for p close to 1. Even if uncertainties do not allow to identify precisely a different plateau for $p \gtrsim 0.55$, the deviation from the homopolymer theta point universality class is very clear. This evidence is enforced by further results for the crossover exponent ϕ_θ defined by $\frac{d}{dT} \overline{\langle R_N^2 \rangle} |_{T=T_\theta} \sim N^{\phi_\theta + 2\nu_\theta}$ and extrapolated from our determinations of this derivative at T_θ . The pattern is qualitatively similar to that of Fig.1. A plateau ($\phi \sim 0.45$) slightly above the exact homopolymer $\phi_\theta = 3/7$ [6] is seen also in this case for $p < 0.50 \div 0.60$, while for $p \gtrsim 0.60$ again clear increasing deviations from this value occur.

The above deviations for $p \gtrsim 0.50$, combined with $T_\theta \sim T_{a\theta}$, suggest that, in the upper range of p , T_d should be very close to, and possibly coincide with T_θ . A strict coincidence is the most plausible way in which disorder could affect the universal theta point properties, while leaving $T_\theta = T_{a\theta}$. Quite remarkably our determinations of T_d based on extrapolations of $\gamma - \gamma_1$ and $\gamma_a - \gamma_{a1}$ are pretty consistent with this conclusion. These exponents are plotted in Fig.3 for $p = 0.6$. T_d corresponds

to the splitting of the two curves, which occurs slightly below T_θ . Although uncertainties are not small, $T_d \sim T_\theta$ is clearly suggested by the overall pattern of determinations (Fig.2) for $p \gtrsim 0.5$, while for $p \lesssim 0.5$ one definitely finds $T_d < T_\theta$, consistent with the picture conjectured above.

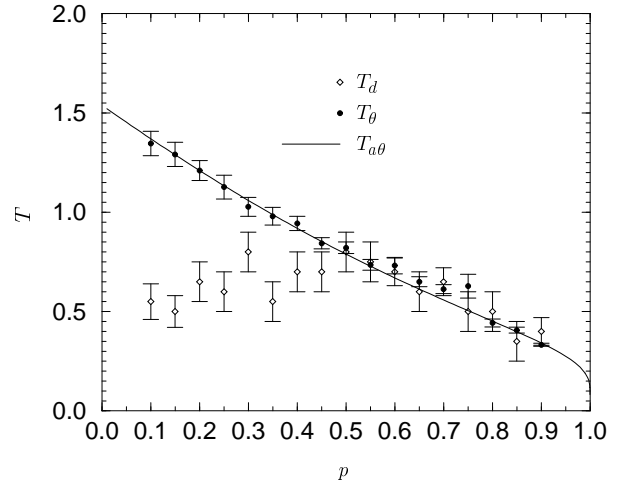


FIG. 2. Temperatures playing a role in the problem.

Frustration is essential in order to produce the above change of theta universality class: distributions $P(V_{ij})$ with support restricted to attractive potentials did not show such modification. Thus, the change from low- to high- p theta regimes could have analogies with a transition from ferromagnetic to spin glass ordering [1].

Summarizing, we gave strong evidence that a sufficient amount of frustrated sequence disorder can be relevant for the heteropolymer behavior in the whole range $T \leq T_\theta$, determining in particular a universality class different from that of homopolymers for the theta transition. This is strongly suggested by the global consistency of our results for various exponents and temperatures of both quenched and annealed problems. The conjecture that $T_d = T_\theta$ in the high frustration regime, is rather natural and implies the intriguing possibility that, when frustration is high enough, specificity becomes a key factor in the quenched statistics right from where the heteropolymer starts collapsing.

The limited accuracy and asymptoticity of our determinations do not allow a precise conjecture on the nature of the transition regime in the whole range $0.50 \lesssim p < 1$. $T_{a\theta}$ approaches 0 very steeply for $p \rightarrow 1^-$ ($T_{a\theta}(p) \sim -1/\log(1-p)$). Also T_d should approach 0 for $p \rightarrow 1^-$ since at all T on the $p = 1$ line the behavior of the system is that of a SAW, controlled by a $T = \infty$ fixed point. The proximity of this line could be responsible for the increase of our ν estimates ($\nu \sim 0.68$) for p closer to 1.

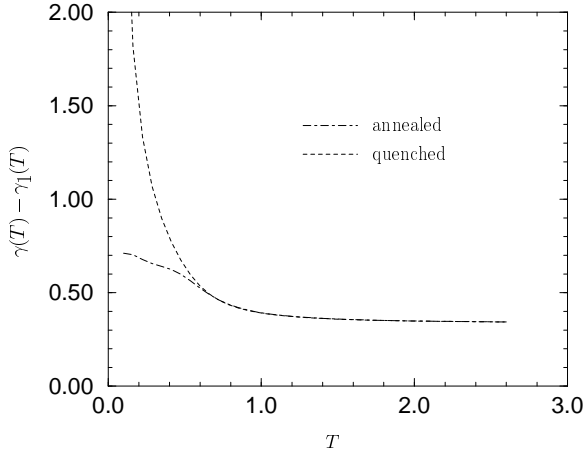


FIG. 3. Example of T_d determination for $p = 0.6$

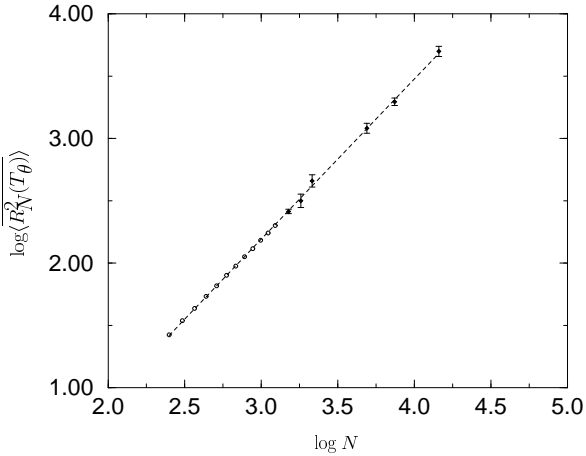


FIG. 4. Exact (empty dots) and MC (full) data for $p = 0.80$.

In order to rule out the possibility that our results could be explained just in terms of a very slow crossover to homopolymer theta behavior, due to the presence of the SAW line, we spent an exceptional effort in extending to larger N by MC methods our determinations of $\overline{R_N^2}$ for the particular case $p = 0.80$. Experience [8,9] has taught us that, besides the difficulty of thermal sampling at low T , which can, e.g., be solved by application of multiple Markov chain algorithms [17], a major limitation of MC in this field is that quenched averages have to be carried out over very large ensembles of chain sequences in order to produce reliable results. This is even more compelling when chain specificity plays a relevant role. By extensive simulations based on a multiple Markov chain method [17] (grids of up to 40 temperatures and ~ 600 different sequences for each N) we obtained extra determinations of $\overline{R_N^2}$ up to $N = 64$. The log-log plot of Fig.4 confirms very nicely the trend of the exact enumeration results and clearly excludes a crossover. On the

basis of all data we could estimate $\nu_\theta(0.8) = 0.64 \pm 0.01$ [18], which qualifies as our best exponent determination concerning the expected novel theta universality class at $p \gtrsim 0.50$. The value of this exponent is surprisingly very close to that appropriate for branched polymers in $2D$ [19].

We expect that the new theta universality class could be found also in more realistic heteropolymer models. Polyampholytes with screened interactions and nonzero total charge [8,20] are good candidates. In general the universality class at the θ point should change as soon as frustration exceeds a certain threshold.

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